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Energy Procedia 14 (2012) 101 – 107

Energy Procedia

2011 2nd International Conference on Advances in Energy Engineering(ICAEE 2011)

Electrical Activation of Nano/Micro-size Crystallite Carbon

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Abstract

Realization of electrical activation of crystallite carbon in electrochemical capacitors has been studied. Constant current charge-discharge and cyclic voltammetry were performed to characterize the electrical activation of crystallite carbon. Results showed that electrochemical capacitor could be activated deeply electrically at high voltage and obtain larger capacitance, yet unstable cycle performance. Electrical activation just takes place in certain current range and the optimized current need to apply for yielding good electrical activation results with large capacitance and stable cycle performance. In further study, it was found that the crucial aspect impacting realization of electrical activation was electric energy.

Keywords: crystallite carbon; electrical activation; PC-based electrolytes

1. Introduction

Electrochemical capacitors get wider and wider application in the world and have become one of the most developing intermediary storage devices due to high-rate characteristics, such as long life, relative higher energy (compared with conventional capacitors) and larger power density(compared with batteries) [1-3]. Therefore, many efforts have been paid to improve the energy density of electrochemical capacitor[4-6], however, the value is still less than 10% of advanced batteries, such as lithium-ion batteries with relative less chargers stored and lower working voltage [7, 8].

Nanogate capacitor using the nanogate carbon as electrodes was reported by Okamura Laboratory [9, 10] and high energy density over 50Wh/kg has been obtained experimentally. Such high energy density was mainly attributed to the capacitor withstanding high voltage and having large capacitance. Electrical activation played an important role in yielding high capacitance, which referred to the co-intercalation of solvent with electrolyte ions into electrode materials under electrical field. After electrical activation, the charge-discharge process liked double layer behavior. The voltage is defined as intercalation starting voltage.

In our study, crystallite carbon was synthesized according to reference. The synthesized crystallite carbon has abundant micro-crystallites with well-grown graphite-like layers and expanded d002 spacing

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doi:10.1016/j.egypro.2011.12.887

between 0.35 and 0.38nm. N_2 adsorption test presents the surface area of CC is less than $100m^2/g$ (BET). Electrochemical capacitor based on crystallite carbon performs the same characteristic as the nanogate capacitor such as, strong capacity withstanding high voltage over 4V, large capacitance deriving from electrical activation and high energy density over 55Wh/kg.

Aimed to modify electrical activation and yield as much capacitance as possible in the prepared electrochemical capacitor, investigation of the best conditions to activate the capacitor electrically is valuable. However, according to the published reports [9,10], seldom discussions relate to electrical activation conditions. Therefore, optimizing electrical activation was been made in this work to find tthe main optimized conditions were needed to realize electrical activation with good cycle performance.

2. Experimental

Crystallite carbon power, black carbon and PTFE were mixed in a mass ratio of 1:0.08:0.04 and dissolved in 50% ethanol solution. The slurry was rolled in a heat board into a sheet with thickness ranging from 0.33-0.35mm, then it was dried at 160℃under vacuum condition for 6 hours. The obtained film was cut into round electrode with diameter of 13mm, and then it was pressed and immersed in 1mol/L Et4NBF4/PC solution. Electrodes and separator was ordered as hamburger type, and healed. XRD was carried out over the 2θ range from 2 to 90 degree using a Rigaku D/ max-A CuKα radiation. Electrochemical tests like constant-current charge–discharge, cyclic voltammetry (CV) and electrochemical impedance spectrum (EIS) measurement were adopted to test the electric characteristics of the electrochemical capacitors. Constant current charge–discharge tests were performed with LAND BT-10 tester in a voltage range of 0–4.5V. Normally, Current density for charging-discharging was set on $4mAcm^{-2}$ except high current tests. Energy (E) delivered during the discharge was calculated according to E = (1/2) CV2, where V stands for the usable voltage. Cyclic voltammetry was executed in model with scan rate of 1mV/s versus Pt as reference electrode.

3. Results and discussion

3.1 Electrical activation of crystallite carbon

The SEM image of synthesized crystallite carbon is shown in Fig.1. The synthesized powders ranged of micro-scale with loose microstructure characteristic. It can be obviously noticed that the active particles distributed in the middle of wadding carbon black powders, and arachnoid PITE fibre connected all these grains.

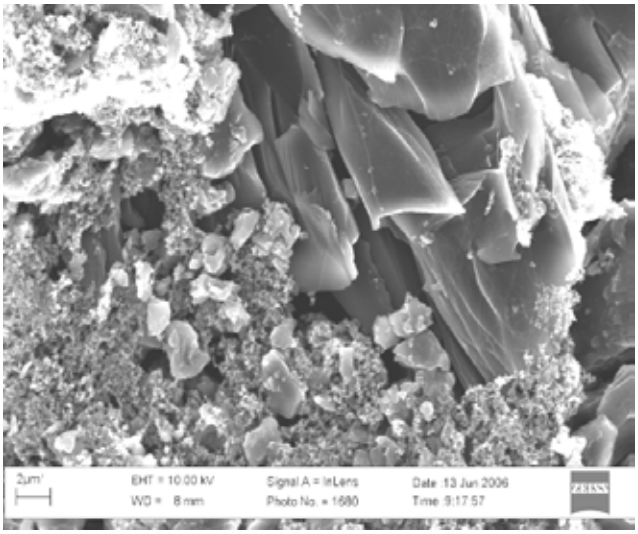

Fig.1. SEM image of crystallite carbon

Fig.2 shows the constant current charge-discharge plots of crystallite carbon electrochemical capacitor at 4V in different cycles. It is clear that in the 1st cycle, the charge line is almost vertical at the beginning of charge, which indicates very small capacitance. However, much milder curve appeared around 3.5V, suggesting the capacitance is increasing. The voltage that the charge line starts to tend to mild is the intercalation starting voltage. In the second and following cycles, perceptible slope change in the charge process was still observed, which implies electrical activation takes place continuously and the capacitance is developed. Finally, the capacitor would work as an electric double-layer capacitor, as revealed in the 55th cycle.

The structural change of crystallite carbon after electrical activation was studied by X-ray diffraction patterns in Fig.3, in which raw electrode was shown in curve ‘a’ and electrode that was activated by voltage of 4V and current of 4mA/cm2 was presented in curve ‘b’. it is clear that strong peak at 2θ=25.073 in curve ‘a’ that reflects the distance of d002 was split after electrical activation and a relative strong new peak appears in the lower angle side at 2θ=21.989. The new peak means layer distance of d002 of a part of loose structure of electrode expands along with electrical activation. Takeuchi group [9,10] reports that when intercalation starting voltage was achieved, electrolyte ions are intercalated between the layers of the crystallites carbon together with the solvent. Therefore, when crystallite carbon is activated electrically, solvent co-intercalation happens and the layer structure of electrode expands simultaneous. The expanded structure could be preserved after the ions are fully discharged and a considerable amount of ions still remain intercalated, which should make the next intercalation easier in the following charging. Electrolyte ions would repeat insertion and extraction the inter-layers of electrode in cycling.

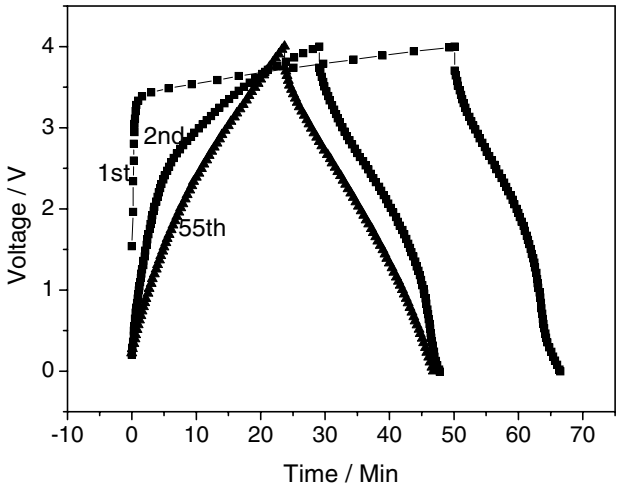

Fig.2 Constant current charge-discharge curves of crystallite carbon in Et_4NBF_4/ PC electrolytes at 4V in different cycle.

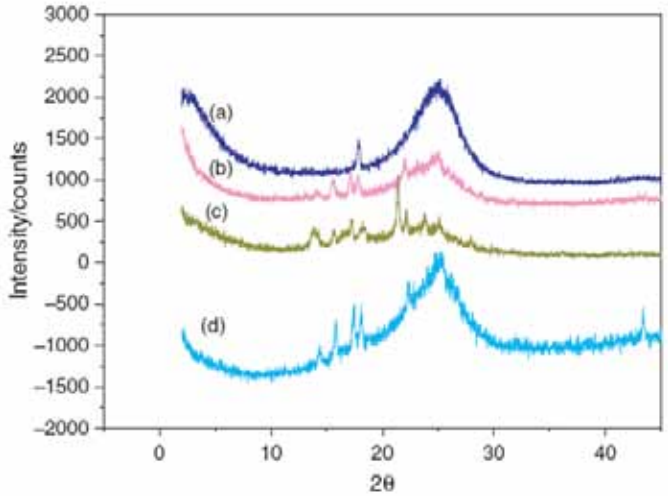

Fig.3. X-ray diffraction spectra of carbons at different conditions a : dry electrode, b: electrode activated electrically by voltage of 4V and current of 4mA/cm^2, c: electrode activated electrically by voltage of 4.5V and current of 4mA/cm^2,d: electrode activated electrically by voltage of 4V and current of 10 mA/cm^2. a sharp line at 2θ=18 is resulting from PTFE binder, and others are not assigned.

3.2 Electrical activation in different electrolytes based on PC solvent

The plots of cyclic voltammetry of positive crystallite carbon electrode in PC-based electrolytes with $LiClO_4$ (a) and Et4NBF4 (b) as salts were shown in Fig.4. From Fig.4 (a), in the first cycle, strong reductive peak appeared at -2.0V and no oxidation current was detected. The reductive current peak could be seen in the following cycles without presenting oxidation current, yet the intensity of reductive peak decreased gradually. This process is agreement with the result of constant current charge-discharge and reflects the micro change in crystallite carbon when it is activated electrically. Discharge capacitance at the first cycle is 68F/g, and then capacitance would be improved in certain cycles and stabilized 99F/g, as revealed in Fig.5.

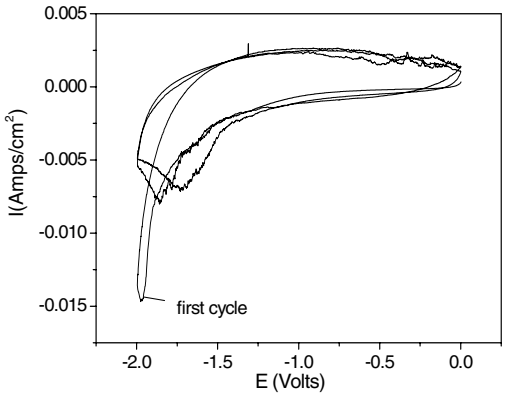

Fig.4(a)

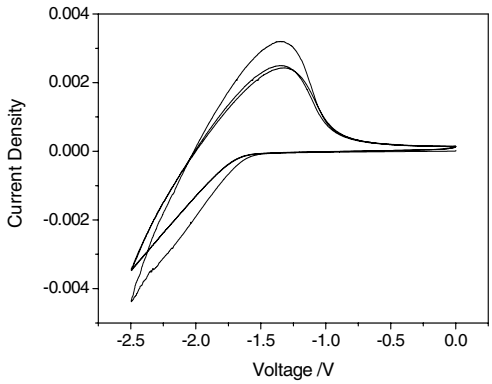

Fig.4(b)

Fig.4 Plots of cyclic voltammetry of positive electrode in PC-based electrolytes with different salts: a: $LiClO_4$; b: Et_4NBF_4. The scan rate is 1mV/s and Pt is reference electrode.

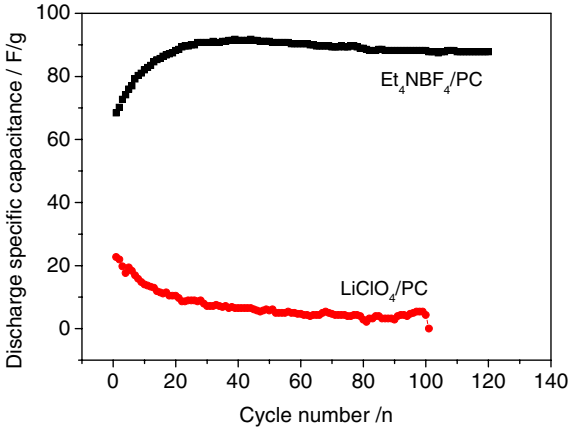

Fig.5. Discharge specific capacitance in cycling in PC-based electrolytes.

However, instead the salt from Et_4NBF_4 to $LiClO_4$, different cyclic voltemmetry behavior was shown in Fig.4 (b). A large reductive current was observed below -1.5V and relative oxidation peak was detected between -1.5V and -1.0V. In the following cycles, reductive current peaks and corresponding oxidation discharge peaks were still observed. This result indicates that intercalation/ de-intercalation of lithium toward crystallite carbon occurred. This process is similar as the mechanism of lithium-ion batteries, and differs from the electrical activation of crystallite carbon since the system cannot work as electric double-layer finally. Discharge Capacitance at first cycle is just 22.68F/g; in the following cycles, the capacitance presents continuous decaying. It is concluded that PC-based electrolyte using $LiClO_4$ as salt was not suitable for activating crystallite carbon.

4. Conclusions

High voltage enhances that the electrochemical capacitor based on crystallite carbon is electrically activated further and brings large capacitance, yet unstable cycle performance. Electrical activation occurs at a certain current range. In the range, moderate current should be chosen to obtain good electrical activation results with larger capacitance and stable cycle performance. Electric energy directly induces the occurrence of electrical activation. Electrical activation voltage varies as the change of inputting conditions, but electric energy is constant when electrical activation takes place.

Acknowledgements

The authors would like to acknowledge financial support provided by Social Developmnet Plan of Yun Province China (No.2008cd148), and Department Science Foundation of China (No.210204).

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